Synthesis and Characterization of an Unusual Heterobridged Di-rhodium Complex. X-Ray Molecular Structure of $[Rh_2(\mu\text{-pz})_2I_2(CO)_2(\mu\text{-dppm})]$

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Synthesis and structure in dinuclear metal complexes have attracted much interest in recent years. Rhodium complexes with two *cis*-binucleating nitrogen donors (*e.g.*, pyrazolate or naphthyridine type ligands) have been reported [1, 2]. On the other hand rhodium complexes with two *trans*-μ-bis(diphenylphosphino)methane (dppm) ligands have been thoroughly investigated; among these intense effort has been directed to the class of compounds with so-called 'A-frames' [3]. In this context we have recently described the preparation of new complexes of formula $[Rh_2(\mu\text{-pz})(CO)_2(\mu\text{-dppm})_2]^+$, having the A-frame type structure with the pyrazolate group as bridgehead ligand, and related $[Rh_2(\mu\text{-pz})I_2(CO)_2(\mu\text{-dppm})_2]^+$ derivatives [4]. We now report the preparation and structural characterization of an unusual heterobridged complex that appears to contain the first example of a rhodium–rhodium bond bridged by only one dppm group and two *exo*-bidentate nitrogen donor ligands.

A diethyl ether or hexane solution of the $[Rh_2(\mu\text{-pz})_2(CO)_4]$ complex (**I**) (pz = pyrazolate) [ν(CO) = 2022, 2079 and 2090 cm^{-1}] [1a] adds successively molecular iodine (1:2 mol ratio) leading to a 2:1 adduct of formula $[Rh_2(\mu\text{-pz})_2I_4(CO)_4]$ (**II**) (80% yield), by the intermediacy of the 1:1 adduct $[Rh_2(\mu\text{-pz})_2I_2(CO)_4]$ (**III**) (65% yield)*. The IR spectrum of complex **III** presents ν(CO) bands at 2088, 2107 and 2120 cm^{-1}; its pattern and the observed shift to higher wavenumbers relative to **I** suggest a two-center oxidative addition with concurrent metal–metal bond formation, as previously observed in a related dinuclear benzamidinate rhodium complex [5]. Complex **II** presents three ν(CO) bands at 2098, 2132 and 2155 cm^{-1}, suggesting the formation of a dinuclear rhodium(III) complex by breaking of the metal–metal bond proposed for complex **III**.

Interestingly, the addition of dppm to a solution of $[Rh_2(\mu\text{-pz})_2I_2(CO)_4]$ (1:1 mol ratio) gives rise to the displacement of carbon monoxide and formation of $[Rh_2(\mu\text{-pz})_2I_2(CO)_2(\mu\text{-dppm})]$ (**IV**) (ν(CO): 2060 cm^{-1}). Its ^{31}P NMR spectrum shows a symmetric multiplet (AA'XX' system) with δ(P) at 28.9 ppm [$^1J(Rh–P) + {}^xJ(Rh–P)$ = 110 Hz]. In order to confirm the proposed formulation of this unusual complex and the relative disposition of the bridging ligands, an X-ray structural determination of **IV** was undertaken. Crystal data: $C_{33}H_{28}I_2N_4O_2P_2Rh_2$, M = 1034.18, Monoclinic, space group $P2_1/n$, a = 12.772(5), b = 24.201(9), c = 11.599(6) Å, β = 96.04(3)°, V = 3565(3) Å^3, D_c = 1.927 g cm^{-3}, Z = 4, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 27.48 cm^{-1}. 5695 independent reflections were collected on a Siemens AED diffractometer ($3 \leqslant \theta \leqslant 24°$). The crystal structure was solved by Patterson and Fourier methods. The refinement was carried out by means of full-matrix least-squares with anisotropic thermal factors for the Rh, I, P, N, O and carbonyl C atoms. The current R value was 0.046 for 2539 observed reflections, having $I \geqslant 2\sigma(I)$. The final atomic coordinates for the non-hydrogen atoms are given in Table I. Thermal parameters and a list of structure factors are available from the authors on request.

The structure of complex **IV** consists of binuclear rhodium(II) complexes triply bridged by two pyra-

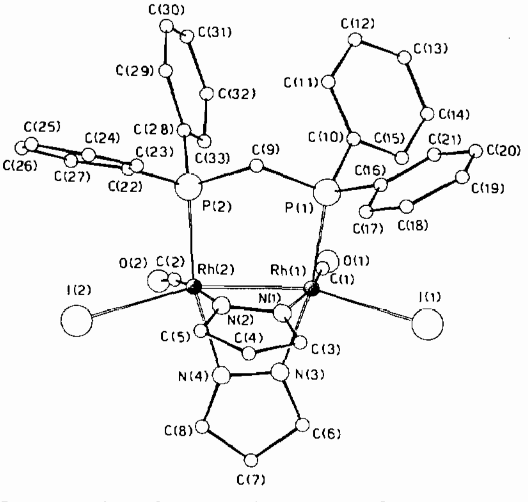

Fig. 1. A view of the complex $[Rh_2I_2(CO)_2(\mu\text{-pz})_2(\mu\text{-dppm})]$ (**IV**). Selected bond distances (Å) and angles (°) are: Rh(1)–Rh(2) 2.612(3), Rh(1)–I(1) 2.710(3), Rh(1)–P(1) 2.288(4), Rh(1)–N(1) 2.039(12), Rh(1)–N(3) 2.076(12), Rh(1)–C(1) 1.85(2), Rh(2)–I(2) 2.736(3), Rh(2)–P(2) 2.284(4), Rh(2)–N(2) 2.036(12), Rh(2)–N(4) 2.139(12), Rh(2)–C(2) 1.83(2); P(1)–Rh(1)–N(1) 89.5(3), P(1)–Rh(1)–N(3) 168.8(4), P(2)–Rh(2)–N(2) 89.4(4), P(2)–Rh(2)–N(4) 166.0(4).

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*All compounds gave satisfactory microanalytical data and molecular weight measurements.

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TABLE I. Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.s in Parentheses for the Non Hydrogen Atoms.

Atom	*x/a*	*y/b*	*z/c*
RH1	334(1)	1654(1)	3329(1)
RH2	1819(1)	971(1)	2871(1)
I1	−1251(1)	2403(1)	3082(1)
I2	3176(1)	388(1)	1658(1)
P1	1224(3)	2075(2)	4905(3)
P2	2908(3)	1209(2)	4483(3)
O1	−886(10)	854(6)	4635(11)
O2	1088(14)	−134(6)	3565(13)
N1	1281(9)	2049(5)	2283(9)
N2	2115(9)	1715(5)	2152(9)
N3	−189(10)	1209(6)	1849(10)
N4	554(11)	896(5)	1517(10)
C1	−395(12)	1174(8)	4196(13)
C2	1367(17)	304(8)	3380(17)
C3	1303(11)	2479(6)	1542(13)
C4	2180(14)	2412(7)	931(15)
C5	2655(12)	1929(7)	1318(13)
C6	−1105(15)	1131(8)	1124(16)
C7	−831(15)	732(8)	326(16)
C8	215(14)	610(7)	620(16)
C9	2622(12)	1918(6)	4905(13)
C10	800(12)	1892(6)	6295(13)
C11	1511(14)	1745(7)	7242(15)
C12	1137(15)	1656(8)	8349(17)
C13	75(17)	1696(8)	8427(18)
C14	−627(17)	1807(9)	7484(19)
C15	−268(14)	1910(7)	6361(16)
C16	1210(11)	2840(6)	4900(12)
C17	1696(13)	3117(7)	4041(14)
C18	1669(14)	3682(7)	4041(15)
C19	1152(14)	3982(7)	4842(15)
C20	659(14)	3689(8)	5684(16)
C21	701(14)	3112(8)	5720(15)
C22	4291(12)	1236(6)	4257(12)
C23	4780(13)	1716(7)	3995(14)
C24	5836(14)	1723(7)	3756(15)
C25	6413(16)	1234(9)	3844(17)
C26	5925(19)	740(10)	4092(20)
C27	4819(16)	721(8)	4313(17)
C28	2859(11)	822(6)	5814(12)
C29	3731(14)	888(8)	6695(16)
C30	3643(18)	607(9)	7764(19)
C31	2792(17)	332(8)	7987(18)
C32	1923(15)	275(7)	7141(16)
C33	1974(13)	522(7)	6035(14)

zolate and one dppm ligands (Fig. 1). Each rhodium atom is octahedrally coordinated and is bound to a iodine atom, to a carbonyl carbon, to a phosphorus from dppm ligand, to two nitrogen atoms from two pyrazolate ligands, and to the other rhodium atom. The Rh–Rh distance [2.612(3) Å] is very short and is comparable with that [2.612(1) Å] reported for the also triply bridged binuclear complex [Rh_2Cl_2(μ-CO)(μ-$Ph_2PPy)_2$] (Ph_2PPy = 2-(diphenylphosphino)-pyridine) [6].

Noteworthy is the mutual disposition of the three ligands in **IV**. The two pyrazolate ligands are nearly perpendicular to each other (the dihedral angle being 97.1(6)°). One of the pyrazolate ligands is also nearly perpendicular to the mean plane passing through Rh(1), Rh(2), P(1), P(2) and C(9), whereas the other is nearly coplanar (dihedral angles 99.9(3) and 7.4(5)° respectively). Dihedral angles not very different are those formed by the mean planes through Rh(1), Rh(2), N(1), N(2) and through Rh(1), Rh(2), N(3), N(4) and that through Rh(1), Rh(2), P(1), P(2), C(9) (86.6(1) and 2.6(2)° respectively).

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